



# Kinetics of oxidative degradation/mineralization pathways of the phenylurea herbicides diuron, monuron and fenuron in water during application of the electro-Fenton process

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## ABSTRACT

The electrochemical advanced oxidation method “electro-Fenton process” has been applied to three phenylurea herbicides, namely diuron, monuron and fenuron. The reactivity of these phenylurea herbicides toward hydroxyl radicals has been found to depend on the number of chlorine substituents of the aromatic cycle. The degradation reaction rate constants ranged from  $4.8 \times 10^9$  to  $12 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , and increased in the following order: diuron (2 Cl) < monuron (1 Cl) < fenuron (no Cl). In this work, we have also investigated the mineralization of aqueous solutions of these herbicides in term of chemical oxygen demand (COD) abatement and mineralization degree larger than 90% for a 3 h treatment time was found. Several aromatic by-products, mainly formed by oxidation of the N-terminal group, accompanied by hydroxylation of the aromatic cycle and/or side methyl group, and aromatic dehalogenation, have been identified. Further steps involved the oxidative opening of the aromatic ring, leading to carboxylic acids and inorganic ions.

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## 1. Introduction

Pollution of surface waters and waste waters by pesticide residues mainly resulting from agriculture activities and pesticide manufacturing plants has strongly increased since several decades. Nowadays, it constitutes a very serious environmental problem for the human health and the ecosystems. To address this problem, the European Union (EU) has implemented programs in order to develop suitable technologies devoted to strongly reduce the pesticides residues in drinking waters. The pesticide standard for drinking water has been set by EU at maximum permissible concentrations of  $0.1 \mu\text{g L}^{-1}$  for an individual pesticide and of  $0.5 \mu\text{g L}^{-1}$  for the sum of all present pesticides. Although the amounts of these substances detected in drinking water are generally inferior to the standards established by EU, waste waters from agricultural and/or industrial activities often contain too high levels of contamination.

Recently, in the framework of various methods developed for destruction of organic pollutants in water, we have proposed an electrochemically induced advanced oxidation process, the electro-Fenton method, as an alternative, very efficient system of water treatment [1–7]. It is based on the action of very reactive hydroxyl

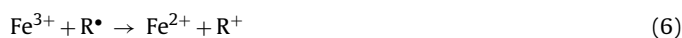
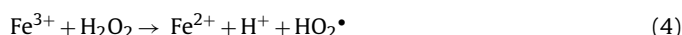
radicals, produced by the Fenton's reagent, which is itself electrochemically generated *in situ*. In this process, molecular oxygen and ferric ions are simultaneously reduced at the cathode to generate hydrogen peroxide and ferrous ions according to the following reactions:



Then, the classical Fenton's reaction takes place in solution and generates radicals ( $\bullet\text{OH}$ ):



The ferrous ions consumed by the Fenton's reaction are regenerated electrocatalytically by reaction (2). Therefore, the Fenton's reagent ( $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$ ) used in this reaction is electrochemically generated *in situ* and by a catalytic way. In these conditions, the Fenton's reaction continues to occur *via*  $\text{Fe}^{2+}$  regeneration according to the reactions (4)–(6) in homogeneous medium, the electrochemical regeneration remaining the major regeneration way.



with  $\text{R}\bullet$  = alkyl radical.

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Thus, no chemical was introduced into the wastewater to be treated, since the reagents of the Fenton's reaction are either *in situ* electrogenerated ( $\text{H}_2\text{O}_2$ ) or electroregenerated ( $\text{Fe}^{2+}$ ) according to a controlled and continuous way. The electro-Fenton process has been efficiently applied to the treatment of many pollutants, including phenols [8,9], synthetic dyes [10–16], herbicides and pesticides [17–20], drugs [21–23] and real wastewaters [24–26].

Phenylurea herbicides are generally applied for the pre- and post-emergence control of weeds in many crops and also on non-cultivated area such as roads and railways. They act as inhibitors of the photosynthesis. Because of their relatively long lifetimes in the environment, these herbicides can be found as contaminants in the surface and ground waters [27]. As a consequence, several research groups have proposed a variety of oxidation methods for degrading and destroying different phenylurea herbicides [28–45]. The ozonation of diuron and other phenylurea herbicides by  $\text{O}_3$  and  $\text{O}_3/\text{H}_2\text{O}_2$  in water has been investigated, the formation of by-products and the degradation pathways being more particularly explored [28]. Upelaar et al. [29] have proposed the use of the Fenton process as a realistic alternative to the  $\text{O}_3/\text{H}_2\text{O}_2$  treatment. The kinetics of oxidation of phenylurea herbicides and chlorobenzenes by the Fenton's reagent ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ ) were also studied [30]. The degradation of diuron, photoinduced by iron(III) and iron/oxalate system in aqueous media, was investigated by Mazellier et al. [31]. Also, the photocatalytic transformation of monuron, fenuron and diuron by  $\text{TiO}_2$  in aqueous solutions as well as the formation of toxic intermediates in the case of diuron have been examined [32–34]. Malato et al. [35,36] have evaluated the technical feasibility, mechanisms, and performances of photocatalytic degradation of aqueous diuron and other water-soluble pesticides by solar photocatalysis, using either heterogeneous photocatalysis with  $\text{TiO}_2$  or homogeneous photocatalysis based on the photo-Fenton reaction. In other related studies, the quantum yields and rates of photolysis of diuron in the presence and absence of  $\text{H}_2\text{O}_2$  [37], the effect of pH on the kinetics of chemical degradation of diuron in water [38], and the kinetics and efficiencies of decomposition of fenuron by means of the photo-Fenton reaction and other photo-oxidation systems [39] have been determined. Also, Losito and co-workers [40–42] have studied the photocatalytic degradation and the electro-Fenton oxidation of several phenylurea herbicides, including isoproturon, chlortoluron and chloroxuron, and have characterized the formed by-products by liquid chromatography–electrospray ionization tandem mass spectrometry. Recently, we have investigated the degradation of diuron, the formation of metabolites, and the evolution of its toxicity in aqueous medium by applying the electro-Fenton process [43,44].

In the present work, our main goals are to determine the kinetics of degradation in acidic aqueous solutions of three phenylurea herbicides, namely diuron, monuron and fenuron, by the electro-Fenton method, to identify their degradation by-products, and to quantitatively study the efficiency of the mineralization process.

## 2. Experimental

### 2.1. Chemicals

The pesticides, including diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], monuron [3-(4-chlorophenyl)-1,1-dimethylurea] and fenuron [3-phenyl-1,1-dimethylurea] (Pestanal<sup>®</sup> grade), and benzoic acid (analytical grade) were purchased from Riedel-de-Haën and used without further purification. Ultra-pure water obtained from a Millipore Milli-Q system with resistivity  $>18\text{ M}\Omega\text{ cm}$  at room temperature was utilized for the preparation of all working solutions and HPLC and LC–MS eluents. Methanol, formic acid (Chromanorm grade) and sulphuric acid were supplied

by VWR International. Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), ferrous sulphate [ $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ] and ammonium iron (II) sulphate hexahydrate [Mohr salt,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ] were purchased from Aldrich.

### 2.2. Instrumentation and procedure

For the electrolysis and electrical charge ( $Q$ ) measurements, a potentiostat-galvanostat EG&G, model 273A, was utilized. Electrolysis was carried out in a non divided, 150 mL electrochemical cell equipped with a carbon felt cathode of  $15\text{ cm}^2$  (Carbon Lorraine), and a Pt anode of  $2\text{ cm}^2$  (Radiometer). The electrochemical degradation of the herbicide aqueous solutions (pH adjusted to 3.0) was carried out at room temperature under current-controlled electrolysis conditions, at various constant current intensity values ( $I = 30\text{--}300\text{ mA}$ ). A moderate compressed air flow was sent throughout the treated solutions during 5 min prior to the electrolysis. A catalytic amount (0.2 mM) of ferrous sulfate [ $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ] was added to the solutions under study before starting the electrolysis.

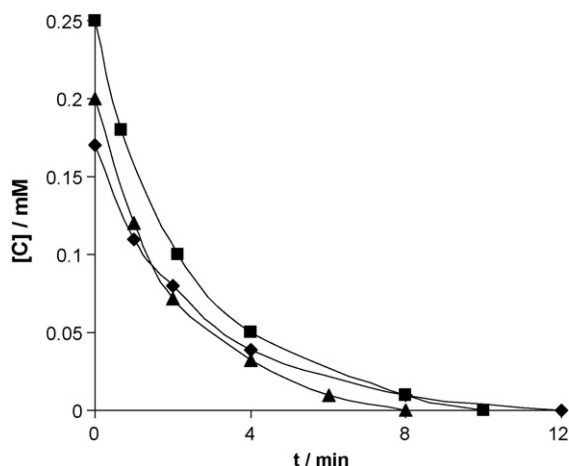
The formation of the herbicide reaction intermediates during electrolysis was monitored by high performance liquid chromatography (HPLC), using a Merck Lachrom chromatograph, equipped with a reversed-phase column (Purospher RP-18;  $5\text{ }\mu\text{m}$ ;  $4.6\text{ mm} \times 250\text{ mm}$ ; Merck), and a diode array detector (model DAD L-7455). The sample volumes were  $20\text{ }\mu\text{L}$ . A water/methanol 40:60 (v/v) mixture was used as elution solution at a flow rate of  $0.7\text{ mL min}^{-1}$ .

The decay of diuron and fenuron, and the evolution of their hydroxylated derivatives were also followed by liquid chromatography–mass spectrometry (LC–MS). The characterization of the diuron and fenuron degradation by-products was performed on a HPLC apparatus (Perkin Elmer 200LC) coupled to an Applied Biosystems API 100 mass spectrometer with an APCI interface (Heated Nebulizer), in the positive mode. The chromatograph was equipped with a Purospher RP-18 column ( $4.6\text{ mm} \times 250\text{ mm}$ ;  $5\text{ }\mu\text{m}$ ; Merck) and an intermediary UV detector (Applied Biosystems 785 A) fixed at  $254\text{ nm}$ . The column was thermostated at  $40^\circ\text{C}$  and the injected volume was  $20\text{ }\mu\text{L}$ . The column was eluted with a mixture of methanol/water/formic acid (60:39.9:0.1, v/v/v), using a flow rate of  $1.0\text{ mL min}^{-1}$ . Mass spectra were collected in the full-scan mode by scanning over a mass range of 145–266 amu in 6 s with a resolution value of 44. The ionization was performed in the APCI-positive mode with the following parameters: ion transfer capillary temperature =  $220^\circ\text{C}$ ; capillary voltage =  $3.5\text{ kV}$ ; cone voltage =  $30\text{ V}$ ; APCI vaporizer temperature =  $400^\circ\text{C}$ ; sheath gas flow =  $8\text{ L min}^{-1}$ ; corona discharge intensity =  $4\text{ }\mu\text{A}$ .

Carboxylic acids were identified by ion-exclusion HPLC chromatography using a Merck Lachrom liquid chromatograph equipped with an L-2130 pump, fitted with a C18 Acclaim OA (i.e., organic acid),  $4\text{ mm} \times 250\text{ mm}$  (i.d.) column at  $30^\circ\text{C}$ , and coupled with a L-2400 UV detector selected at  $\lambda = 210\text{ nm}$ . A  $100\text{ mmol L}^{-1}\text{ Na}_2\text{SO}_4$  (adjusted at pH 2.65 with methanesulfonic acid) at a flow rate of  $0.2\text{ mL min}^{-1}$  was used as the mobile phase. Measurements were always controlled through an EZChrom Elite 3.1 software.

Dionex ICS-1000 Basic Ion Chromatography System was utilized for the determination of chloride and nitrate anions. The system was fitted with an IonPac AS4A-SC,  $25\text{ cm} \times 4\text{ mm}$  (i.d.), anion-exchange column, linked to an IonPac AG4A-SC,  $5\text{ cm} \times 4\text{ mm}$  (i.d.) column guard. The sensitivity of this detector was improved from electrolyte suppression using an electrochemical self-regenerating suppressor ASRS-ULTRA II. Measurements were conducted with a solution of  $1.8\text{ mmol L}^{-1}\text{ Na}_2\text{CO}_3$  and  $1.7\text{ mmol L}^{-1}\text{ NaHCO}_3$  at  $2.0\text{ mL min}^{-1}$  as the mobile phase.

Chemical oxygen demand (COD) analysis of initial and treated aqueous diuron solution was carried out by means of the AFNOR NPT-90-101 method. For COD analysis, samples were taken from



**Fig. 1.** Kinetic curves of phenylurea herbicide degradation in acid aqueous solution at pH 3.0 and room temperature during the electro-Fenton process. Initial herbicide concentrations:  $[\text{diuron}]_0 = 0.17 \text{ mM}$ ;  $[\text{monuron}]_0 = 0.25 \text{ mM}$ ;  $[\text{fenuron}]_0 = 0.20 \text{ mM}$ ,  $I = 100 \text{ mA}$ ,  $[\text{Fe}^{3+}] = 0.2 \text{ mM}$ ,  $V = 125 \text{ mL}$ .

the reaction mixture at different electrolysis times and were micro-filtered onto a hydrophilic membrane (Millex-GV Millipore; pore size =  $0.22 \mu\text{m}$ ). The organic matter was oxidized in concentrated  $\text{H}_2\text{SO}_4$  solution by potassium dichromate under energetic conditions. The temperature of the solution was raised from about  $20^\circ\text{C}$  to  $170^\circ\text{C}$  within 2 h. The excess of potassium dichromate was measured by Mohr salt titration.

### 3. Results and discussion

#### 3.1. Kinetic study of the phenylurea herbicide degradation

We investigated the kinetics of degradation of the three phenylurea herbicides (diuron, monuron and fenuron) occurring during the electro-Fenton process. The degradation kinetics experiments were performed at room temperature in diluted acidic (pH 3.0) aqueous solutions of herbicides (initial concentrations =  $0.17\text{--}0.25 \text{ mM}$ ), containing catalytic amount of ferric ions. The decay of initial herbicide concentration was monitored by HPLC. As can be seen in Fig. 1, the kinetic curves of herbicide degradation, obtained for  $I = 100 \text{ mA}$  and in the presence of  $[\text{Fe}^{3+}] = 0.2 \text{ mM}$ , were characterized by a regular and relatively fast exponential decrease of the herbicide concentration with the electrolysis time. The final herbicide concentrations, reached after 5–12 min according to the herbicide and the experimental conditions, were around  $10^{-6} \text{ M}$ .

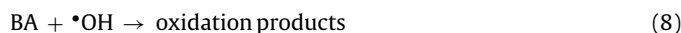
Also, it is worthwhile to note that the degradation rate depended on the number of chlorine atoms of the aromatic cycle. Indeed, we found that diuron (containing two chlorine atoms) was degraded more slowly than monuron (with one chlorine atom). The degradation rate of fenuron (without chlorine atom) was significantly larger than that of the two other herbicides. A similar behaviour has been also observed during the hydroxylation of chlorophenols [45].

Under the above-mentioned standard experimental conditions, the rate of production of the hydroxyl radicals ( $\bullet\text{OH}$ ) is electrochemically controlled and can be assumed to be practically constant. Moreover, since the  $\bullet\text{OH}$  radical constitutes very reactive chemical species (very short lifetime), their destruction rate is very high, and they cannot accumulate in the reaction medium. Therefore, the concentration of hydroxyl radicals can be considered as practically constant, and the quasi-stationary state kinetic hypothesis can be applied to their concentration [46]. Consequently, we can assume that the hydroxylation reaction of phenylurea her-

bicides (PHU) with  $\bullet\text{OH}$  (reaction (7)) obeys a pseudo-first-order kinetic.



The PHU hydroxylation absolute rate constants can be evaluated by taking the reaction of benzoic acid (BA) with  $\bullet\text{OH}$  (reaction (8)) as a standard, and by performing a kinetic measurement of the competitive decay of BA and PHU under standard experimental conditions. This reaction has been chosen because the BA hydroxylation absolute rate constant value ( $k_{\text{BA}} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) is well documented [47].



Considering the first minutes of the treatment and assuming that no side-reaction of the phenylurea herbicides or of the reference compound (BA) occurred, we applied the pseudo-first-order integrated kinetic Eq. (9) to determine the hydroxylation absolute rate constants of phenylurea herbicides [45]:

$$\ln \frac{[\text{PHU}]_0}{[\text{PHU}]_t} = \frac{k_{\text{PHU}}}{k_{\text{BA}}} \ln \frac{[\text{BA}]_0}{[\text{BA}]_t} \quad (9)$$

where  $k_{\text{PHU}}$  and  $k_{\text{BA}}$  represent, respectively, the second-order hydroxylation absolute rate constants of the phenylurea herbicides under study and of benzoic acid, and the subscripts 0 and  $t$  correspond, respectively, to the reagent concentrations at time  $t = 0$  (initial concentration) and at any time  $t$  of the reaction. A plot of  $\ln([\text{PHU}]_0/[\text{PHU}]_t)$  vs.  $\ln([\text{BA}]_0/[\text{BA}]_t)$  provided a linear relationship, the slope representing the ratio of rate constants ( $k_{\text{PHU}}/k_{\text{BA}}$ ), from which the  $k_{\text{PHU}}$  value could be calculated.

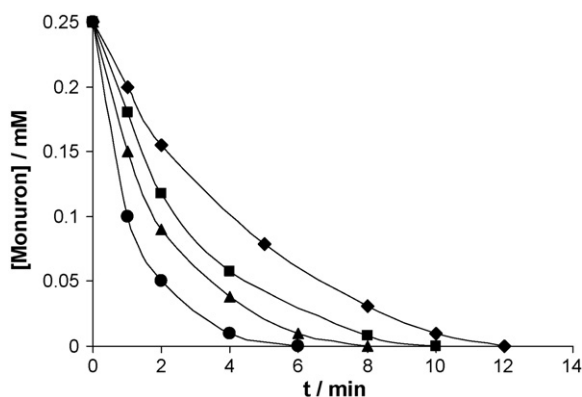
Using this method, we found  $k_{\text{PHU}}$  absolute rate constant values respectively equal to  $4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for diuron,  $7.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for monuron, and  $12 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for fenuron. As already stated in the study of the degradation rates, the  $k_{\text{PHU}}$  values significantly decreased with the increasing number of chlorine atoms of the aromatic cycle. This behaviour can be related to steric and/or electron-withdrawing substituent effects of aromatic chlorine on the rate constants.

Our  $k_{\text{PHU}}$  value for diuron appeared in rather good agreement with those found by Gallard and De Laat [30] for the chemical oxidation of diuron with the Fenton's reagent ( $6.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), and by Djebbar et al. [37] for the photolysis of diuron in the presence of  $\text{H}_2\text{O}_2$  ( $4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). In the case of monuron, our  $k_{\text{PHU}}$  value was very close to that of  $6.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  obtained by Tahmasseb et al. [28] by the ozonation of this compound in presence of  $\text{H}_2\text{O}_2$ . No absolute rate constant literature value was reported for fenuron degradation. These very large hydroxylation absolute rate constant values, close to the diffusion rate constants in solution, demonstrate the very high reactivity of hydroxyl radicals toward phenylurea herbicides, in good accord with the results reported for the oxidation of other organic pollutants [47,49].

#### 3.2. Effect of the experimental conditions on degradation efficiency

In order to determine the efficiency of the electro-Fenton process under different experimental conditions, the influence of several experimental parameters, such as the applied current intensity and the catalyst concentration, upon the phenylurea herbicide degradation rate was also investigated.

The phenylurea herbicide diluted acid aqueous solutions were electrolyzed at a constant applied current ranging between 60 and 300 mA, at pH 3.0, in the presence of  $[\text{Fe}^{3+}] = 0.2 \text{ mM}$ , and at room temperature. An example of kinetic curves of degradation is shown for monuron in Fig. 2. It can be observed that the degradation rate significantly increased with the applied current intensity. Similar results were obtained for the other compounds.

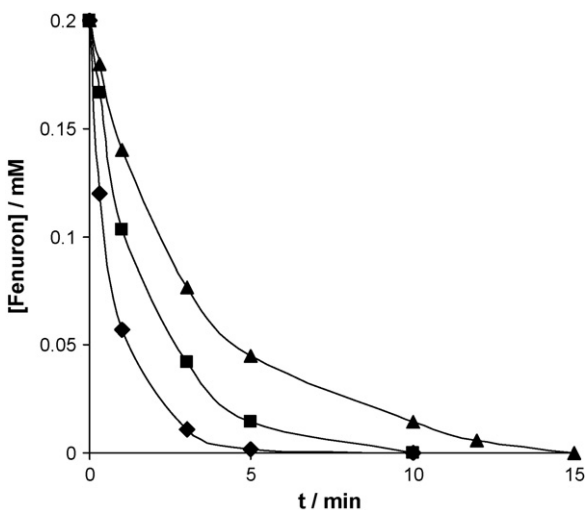


**Fig. 2.** Effect of the applied current intensity on the kinetic curves of the monuron degradation in acid aqueous solution (pH 3.0) at room temperature during the electro-Fenton process.  $I$  (mA): 60 (♦); 100 (■); 200 (▲) and 300 (●). Operating conditions:  $[\text{monuron}]_0 = 0.25$  mM,  $[\text{Fe}^{3+}] = 0.2$  mM,  $V = 125$  mL.

This degradation rate increase can be attributed to the augmentation of the production rate of  $\text{H}_2\text{O}_2$ , and to the acceleration of the catalytic cycle  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , which would lead to enhance the rate of formation of the hydroxyl radicals and, consequently, to increase the rate of degradation of phenylurea herbicides.

The phenylurea herbicides solutions were electrolyzed at different catalyst concentrations  $[\text{Fe}^{3+}] = 0.2\text{--}0.5$  mM, at pH 3.0, for  $I = 100$  mA, and at room temperature. The kinetic curves of degradation are presented in Fig. 3 for fenuron. As can be seen, the degradation rate of fenuron significantly decreased with the increase of  $\text{Fe}^{3+}$  catalyst concentration. Similar results were found in the case of the other compounds.

Since the applied current intensity was kept constant at 100 mA in all experiments, it can be assumed that the production rate of  $\text{H}_2\text{O}_2$  via the oxygen reduction should be identical for all the  $\text{Fe}^{3+}$  concentrations under study, whereas the formation rate of  $\text{Fe}^{2+}$  via  $\text{Fe}^{3+}$  reduction should increase due to the increase of the  $\text{Fe}^{3+}$  catalyst concentration. Therefore, the observed decrease in degradation rate upon increasing the  $\text{Fe}^{3+}$  concentration can be attributed to the role of  $\text{Fe}^{2+}$  species as scavenger of the  $\cdot\text{OH}$ . Indeed, in these conditions, reaction (10) between  $\text{Fe}^{2+}$  and  $\cdot\text{OH}$  takes place with a large



**Fig. 3.** Effect of the catalyst ( $\text{Fe}^{3+}$ ) concentration on the kinetic curves of 0.20 mM fenuron degradation in acidic aqueous solution (pH 3.0) during the electro-Fenton process at 100 mA and room temperature.  $C_0$  (mM): 0.2 (♦); 0.5 (■); 0.1 (▲).  $V = 125$  mL.

rate constant ( $k = 3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ):



Due to this very high reactivity, reaction (10) which consumes hydroxyl radicals should become competitive with the other reactions, leading to diminish the degradation rate of phenylurea herbicides.

### 3.3. Analysis of the phenylurea herbicide degradation products

In order to elucidate the phenylurea herbicide degradation mechanism and to characterize the various pathways, it is necessary, in addition to the above-described kinetic study, to precisely identify the by-products formed during the initial part of the electro-Fenton process. The identification of these degradation products also constitutes the key to improving the overall process efficiency. Moreover, since, in general, hydroxyl radicals are reacting non-selectively, a number of by-products are formed at relatively low concentration levels.

For this characterization purpose, we analyzed the evolution of the HPLC peaks corresponding to the phenylurea herbicides and to their by-products, by studying the chromatograms of samples of electrolyzed solutions of phenylurea herbicides, collected within the first 15 min of the electro-Fenton process. The quantitative determination of the phenylurea pesticides by LC–MS using APCI [42] and ESI [43,44] interface being already demonstrated, we used this technique to identify the main intermediate degradation products of diuron and fenuron which are presented in Tables 1 and 2. The three main reaction ways leading to the formation of these products are described below more in detail.

#### 3.3.1. Attack on the N-terminal

This way led to the demethylation of the initial compound and formation of by-products containing a terminal  $-\text{NH}-\text{CH}_3$  group (compounds 2 and 9, Tables 1 and 2). Occurrence of similar products was reported by several authors in the degradation of diuron and monuron by other advanced oxidation processes [28,31,33,35]. A by-product possessing a  $\text{N}(\text{CH}_3)-\text{CO}_2\text{H}$  terminal group was also observed by Richard and Bengana [50] in the photocatalytic degradation of fenuron.

#### 3.3.2. Hydroxylation of the aromatic cycle

As can be seen in Tables 1 and 2, the electro-Fenton oxidation of diuron and fenuron was characterized by a hydroxylation of the aromatic cycle, yielding the compounds 3, 4 and 11, or other position isomeric hydroxylated degradation products. Tahmassebi et al. [28] showed also that, during the ozonation of diuron and other phenylurea herbicides by  $\text{O}_3$  and  $\text{O}_3/\text{H}_2\text{O}_2$  in water, several hydroxylated position isomers were formed, the hydroxylation at the *ortho* position being favoured.

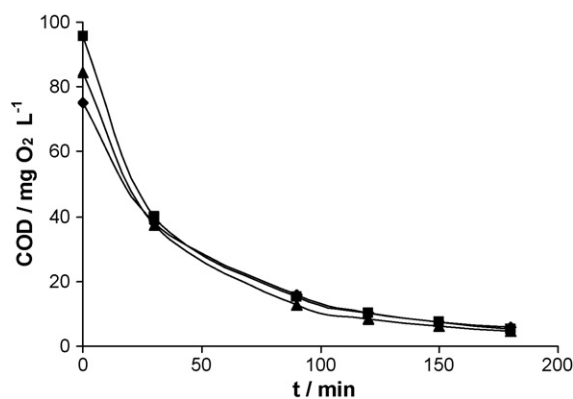
#### 3.3.3. Aromatic dehalogenation and hydroxylation

By-products such as compounds 5 and 6, resulting from the simultaneous aromatic dehalogenation and hydroxylation can be identified with certainty in the case of the diuron herbicide degradation. Tahmassebi et al. [28] found also that the substitution of a chlorine atom by an OH group occurred in the ozonation of monuron and of diuron. Similarly, Jirkovsky et al. [51] observed that the major photoproducts formed in the photolysis of diuron in aqueous solution resulted from the substitution of chlorine by OH.

### 3.4. Study of the mineralization process

To study the extent and the evolution of the mineralization process, we carried out the electrolysis of phenylurea herbicide





**Fig. 4.** COD abatement as function of electrolysis time showing the evolution of mineralization extent of phenylurea herbicides aqueous solutions of pH 3.0 during the electro-Fenton treatment at  $I = 100$  mA and room temperature. [diuron] ( $\blacklozenge$ ) = 0.17 mM; [monuron] ( $\blacksquare$ ) = 0.25 mM; [fenuron] ( $\blacktriangle$ ) = 0.20 mM.  $[\text{Fe}^{3+}] = 0.2$  mM,  $V = 125$  mL.

aqueous solutions during several hours, and we measured the evolution of COD with electrolysis time. The curves of  $[\text{COD}] = f(\text{electrolysis time})$  for the three phenylurea herbicides under the above-described optimal conditions ( $I = 100$  mA;  $[\text{Fe}^{3+}] = 0.2$  mM; pH 3.0) are gathered in Fig. 4. As can be seen, a progressive decrease

of COD is occurring with electrolysis time, the decay rate being approximately similar for the three compounds. The mineralization yield values were 92% for diuron, 92.6% for monuron, and 93.7% for fenuron, at a 3 h electrolysis time, corresponding to an electrical charge about of 1000 C.

For this  $Q$  value, the organic matter still present in the solution was essentially found under the form of short-chain carboxylic acids. The mineralization rate, which was high at the beginning of the treatment, decreased progressively with the electrolysis time towards the end. This rate decrease can be attributed to the transformation of aromatic by-products into aliphatic compounds by aromatic cycle opening reactions [40,52,53]. Since the carboxylic acids formed under these conditions presented generally a poor reactivity toward  $\bullet\text{OH}$ , the mineralization rate decreased significantly at the end of the treatment, as recently reported by Oturan et al. [54].

### 3.4.1. Evolution of the generated carboxylic acids

To gain better insight into the oxidative ability of the electro-Fenton process, we investigated the evolution of the short-chain carboxylic acids generated during the mineralization of phenylurea herbicides. Indeed, the formation of this type of acids has been detected in the mineralization of acid aqueous solutions of aromatic herbicides, using the electro-Fenton reaction [22,45,48,54–56].

**Table 1**  
Identification of the diuron degradation products by LC–MS.

Compound	$t_r^a$ (min)	$[\text{M}-\text{H}]^{+b}$	Identification	Chemical structure
1	14.19	233	3-(3,4-Dichlorophenyl)-1,1-dimethyl urea (diuron)	
2	12.70	219	3-(3,4-Dichlorophenyl)-1,1-methyl urea	
3	9.78	249	3-(3,4-Dichloro-hydroxyphenyl)-1,1-dimethyl urea <sup>c</sup>	
4	3.08	213	3-(Trihydroxyphenyl)-1,1-dimethyl urea <sup>c</sup>	
5	2.84	201	3-(3-Hydroxy-4-chlorophenyl)-1,1-methyl urea <sup>d</sup>	
6	2.33	215	3-(3-Hydroxy-4-chlorophenyl)-1,1-dimethyl urea <sup>d</sup>	

<sup>a</sup>  $t_r$ : retention time.

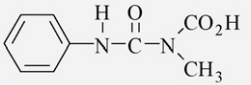
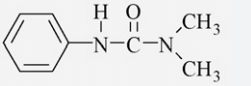
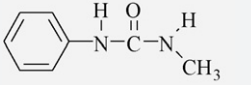
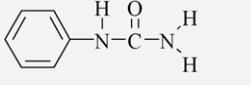
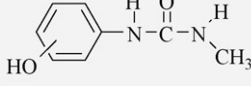
<sup>b</sup> Molecular weight of the corresponding molecular ion.

<sup>c</sup> For these degradation products, the position of hydroxyl group(s) on the aromatic ring or on the side methyl group cannot be attributed with certainty by the LC–MS method, and several position isomeric structures are compatible with the molecular weight of the molecular ion.

<sup>d</sup> For these degradation products, the position of the hydroxyl group on the aromatic ring has been deduced from the simultaneous dehalogenation/hydroxylation occurring during the diuron degradation.

**Table 2**

Identification of the fenuron degradation products by LC–MS.

Compounds	$t_r^a$ (min)	$[M-H]^+b$	Identification	Chemical structure
7	8.24	195	1-Methyl-1-formic acid-3-phenyl urea	
8	7.38	165	1,1-Dimethyl-3-phenyl urea (fenuron)	
9	6.56	156	1-Methyl-3-phenyl urea	
10	5.54	137	3-Phenyl urea	
11	3.22	167	Hydroxyphenyl-1-methyl urea <sup>c</sup>	

<sup>a</sup>  $t_r$ : retention time.<sup>b</sup> Molecular weight of the corresponding molecular ion.<sup>c</sup> For this degradation product, the hydroxyl group position on the aromatic ring or on the side methyl substituent cannot be attributed with certainty by the LC–MS method, and several position isomeric structures are compatible with the molecular weight of the molecular ion.

Under our experimental conditions, we were able to identify by HPLC analysis, with an ion-exclusion column, the formation of formic and oxalic acids in the case of monuron (Fig. 5). Similar results were obtained for diuron and fenuron. Several additional, minor peaks corresponding to other carboxylic acids also appeared in the chromatograms, but could not be characterized, due to the lack of available standard compounds.

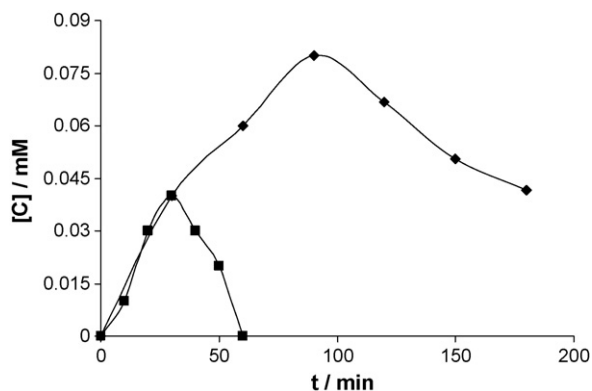
As can be seen in Fig. 5, formic acid reached a maximum concentration for a 30-min electrolysis time of the monuron solutions, and was completely degraded within 60 min, whereas oxalic acid attained a maximum concentration after approximately 90 min of electrolysis, and then was much more slowly degraded, reaching a minimum concentration of about  $5 \times 10^{-5}$  M within about 180 min of treatment. This relatively weak degradation observed for oxalic acid can be attributed to its high stability in the presence of ferric ions, and to its weaker reactivity toward  $\bullet OH$  radicals ( $k = 1.4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ) [47]. The degradation of formic and oxalic acids with time followed a very close behaviour in the case of the

electrolysis of diuron and fenuron. Contrarily to Malato et al. [36] who observed the formation of formic, oxalic and acetic acids in the photo-Fenton reaction of diuron, no acetic acid was detected in our case, probably because of its rapid transformation into oxalic and formic acids. At the end of the electro-Fenton treatment, the small amount of COD remaining in solution (less than  $6 \text{ mg O}_2 \text{ L}^{-1}$ ) was attributed to the presence of oxalic acid traces.

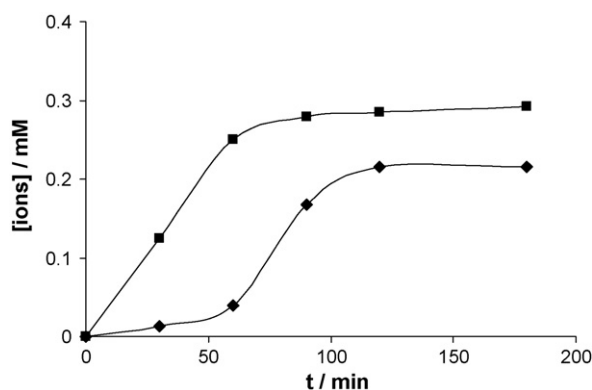
### 3.4.2. Evolution of the chloride and nitrate ions

In the pesticide chemical oxidation by various processes, achievement of mineralization leads to the final formation of carbon dioxide as well as of inorganic ions which result from the initial content of the parent molecules in chlorine and nitrogen atoms [19,45,48,57]. The occurrence of a dechloration step is generally observed in the case of chlorine-containing organic molecules [45,48,58]. Also, Konstantinou and Albanis [59] have shown that the photocatalysis of various classes of pesticides in the presence of titanium oxide led to their degradation in intermediate species and, then, to their mineralization into end-products such as  $\text{Cl}^-$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Similarly, we noted the formation of chloride and nitrate ions during the degradation of phenylurea herbicides by the electro-Fenton process. Fig. 6 shows the evolution of the concentration of chloride and nitrate ions during the electrolysis of diuron.

As can be seen, the release of chloride ions was rapid since a plateau corresponding to a quasi-stoichiometric concentration value ( $\approx 90\%$  of the chlorine atoms initially present in the parent molecule) was reached for diuron after a 90 min treatment. These results indicate that the mineralization of organic chlorine is taking place more rapidly than that of organic carbon. A similar behaviour was observed in the case of monuron. These findings are in good agreement with the results obtained by Pramuro and Vicenti [32] who observed the formation of  $\text{Cl}^-$  and  $\text{NO}_3^-$  during the photocatalytic degradation and mineralization of monuron in aqueous  $\text{TiO}_2$  dispersions, and the observations of Fdil et al. [49] in the case of the mineralization of several chlorophenoxy acid herbicides by means of the photo-Fenton reaction.



**Fig. 5.** Evolution of the concentrations of formic (■) and oxalic (◆) acids during the degradation of monuron in aqueous solution of 0.25 mM of pH 3.0 by the electro-Fenton process at 100 mA and room temperature.  $[\text{Fe}^{3+}] = 0.2 \text{ mM}$ ,  $V = 125 \text{ mL}$ .

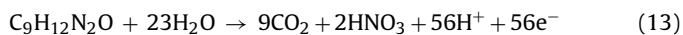
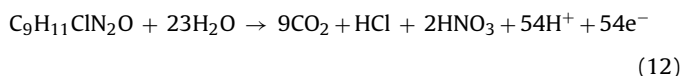
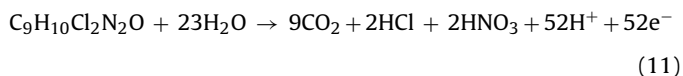


**Fig. 6.** Evolution of the release and accumulation in the medium of chloride (♦) and nitrate (■) ions during the degradation of 0.17 mM diuron aqueous solution of pH 3.0 by the electro-Fenton process at 100 mA and room temperature.  $[\text{Fe}^{3+}] = 0.2 \text{ mM}$ ,  $V = 125 \text{ mL}$ .

In contrast, the release of nitrate ions was much slower, since the stationary state was reached after approximately 120 min of treatment of the diuron solutions (Fig. 5). Moreover, only about 60% of the amount of the nitrogen atoms initially present in the parent molecules were converted into nitrate ions. This mass balance of nitrogen, significantly lower than expected by the reaction stoichiometry, suggests the probable presence of ammonium ions, and also the possible loss of nitrogen under the form of nitrogen oxide ( $\text{NO}_x$ ) species. Similarly, Ammar et al. [46] reported that 45% of the nitrogen content of 2-nitrophenol was converted into  $\text{NH}_4^+$  ions during the electro-Fenton treatment of its aqueous solution.

#### 3.4.3. Apparent current efficiency

Our above-described results indicate that the three phenylurea herbicides under study are quasi-completely mineralized by the electro-Fenton process, carbon dioxide, chloride and nitrate ions being generated. The electrochemical oxidation reactions corresponding to the electrochemical mineralization processes can be written according to reaction (11) for diuron, reaction (12) for monuron, and reaction (13) for fenuron.



These equations involved the consumption of 52, 54 and 56  $\text{F mol}^{-1}$ , respectively, for diuron, monuron, and fenuron. The apparent current efficiency ( $\eta_F$ ) can be determined for all experiences by using Eq. (14).

$$\eta_F = \frac{\Delta(\text{COD})VF}{8I\Delta t} \quad (14)$$

where  $\Delta(\text{COD})$  is the experimental COD decay in solution at a given electrolysis time  $\Delta t$ ,  $I$  is the applied current intensity (A),  $F$  is the Faraday constant (96,487 C), and  $V$  is the electrolytic solution volume (in L).

As shown in Table 3, the  $\eta_F$  values were maximum for a 0.5 h electrolysis time (28–41%, according to the compound), but markedly decreased for a 3 h electrolysis time (11–13%, according to the compound), when more than 90% of mineralization was achieved.

**Table 3**

Evolution of the apparent current efficiency ( $\eta_F$ ) and COD removal percentages for the phenylurea herbicides mineralization by the electro-Fenton process.

Herbicide	Current (mA)	After 0.5 h of treatment		After 3 h of treatment	
		COD removal (%)	$\eta_F$ (%)	COD removal (%)	$\eta_F$ (%)
Diuron	100	49.0	28	92.0	11
Monuron	100	56.0	41	92.6	13
Fenuron	100	56.0	35	93.7	13

These results suggest the existence of a concomitant decay in the oxidative ability of the electro-Fenton system with the electrolysis time, related to the formation of less easy to oxidize by-products, resulting from the decrease of phenylurea herbicide concentrations. The observed decay of mineralization efficiency could be also due to the formation of by-products, such as oxalic acid, that are more difficult to mineralize (Fig. 5).

#### 3.4.4. Mineralization pathway

We were able to propose, in the case of diuron, a mineralization pathway based on the above-described HPLC characterization and evolution of a number of aliphatic and aromatic by-products (Table 1) as well as of inorganic ions. The initial step involved the competitive attack of two different sites of the parent molecule by hydroxyl radicals: (i) addition on the aromatic cycle leading to the formation of product 3. Further oxidation steps resulted into the hydroxylation of the aromatic cycle, followed by the release of chlorine atoms (formation of products 4, 5 and 6), and (ii) abstraction of a hydrogen atom from the dimethylurea group. Then, the formed diuron radical alkyl  $\text{R}^\bullet$  reacted with molecular oxygen to yield  $\text{RO}_2^\bullet$ , and the reaction of  $\text{RO}_2^\bullet$  led to product 2. Interestingly, we also detected by HPLC the formation of the main by-product of diuron degradation, namely 3,4-dichloroaniline, which was identified by comparison with the retention time and UV absorption spectra of the standard, measured under the same experimental conditions. Its presence can be explained by the oxidation of the side chain to a  $-\text{NH}_2$  group. However, we did not found experimental evidence of aniline by-products, probably because of their further rapid degradation.

The final steps of the mechanism were characterized by the oxidative opening of the aromatic cycle leading to the formation of the above-described short-chain carboxylic acids and of inorganic ions. This mineralization pathway of diuron by the electro-Fenton process appears in satisfactory agreement with our experimental results, and could present also the interest to predict the evolution of toxicity during the electro-Fenton treatment, due to the formation of a number of by-products [44]. Moreover, it is worthwhile to emphasize the possibility of extending this mechanism to the degradation and mineralization of monuron and fenuron by the electro-Fenton process.

Therefore, we were able to identify several aromatic by-products, mainly issued from the oxidation of the phenylurea N-terminal group, and accompanied by hydroxylation of the aromatic cycle and substitution of chlorine atoms. Another important result of our study is that the mineralization of these herbicides is characterized by a COD abatement rate larger than 90% for a 3-h treatment time by the electro-Fenton process. The identified reaction intermediates of phenylurea herbicides indicate that the oxidative degradation mechanism is initiated by the attack of the hydroxyl radicals of the parent molecule at two positions, the phenylurea N-terminal group and the aromatic cycle, and leads to several by-products. Further oxidations steps involved the oxidative opening of the aromatic ring, yielding short-chain carboxylic acids and inorganic ions.

#### 4. Conclusions

In this work, we have demonstrated that the degradation kinetics of three selected phenylurea herbicides, including diuron, monuron and fenuron, in acidic aqueous solutions by the electro-Fenton process were function of the number of chlorine atoms substituted on the aromatic cycle. Absolute rate constant values for reactions of phenylurea herbicides with hydroxyl radicals were very high and close to the diffusion rate of reactions in solution, ranging from  $4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  to  $12 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , according to the herbicide. Also, the degradation kinetics markedly depended on the experimental conditions, the rates increasing with the augmentation of applied current intensity, and decreasing with the increase of  $\text{Fe}^{3+}$  (catalyst) concentration.

In addition, we have been able to identify several aromatic by-products, mainly issued from the oxidation of the phenylurea N-terminal group, and accompanied by hydroxylation of the aromatic cycle and substitution of chlorine atoms.

Another important conclusion of our study is that the mineralization efficiency of phenylurea herbicide solutions measured in term of COD abatement was very high since a mineralization degree of 90% was reached after only a 3-h treatment time by the electro-Fenton process.

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